Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 81 (2016) 49 – 52

Physics Procedia

28th International Symposium on Superconductivity, ISS 2015, November 16-18, 2015, Tokyo, Japan

Change of the surface structure by F doping in BiS_2-based superconductor $CeO_{1-x}F_xBiS_2$

S. Demura[a,b,*], Y. Fujisawa[a], T. Machida[c], M. Nagao[d], Y. Takano[b], and H. Sakata[a]

[a]*Tokyo University of Science, Department of Physics, Shinjyuku-ku, Tokyo 162-8601, Japan*
[b]*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[c]*RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*
[d]Yamanashi University, 7-32 Miyamae, Kofu, Yamanashi 400-5811, Japan

Abstract

The observation of the surface structure on single crystalline $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) was performed successfully using a scanning tunneling microscopy. In the sample with x = 0.5, the square lattice composed of Bi atoms was observed. In addition, defects of the surface atoms and streaks were detected on the surface as in the case of $NdO_{0.7}F_{0.3}BiS_2$ single crystal. With further F doping, the surface structure of sample with x = 0.7 showed a novel structure, termed by the "bone" structure. This result suggests that the F concentration affects the surface structure.

Peer-review under responsibility of the ISS 2015 Program Committee

Keywords: Superconductivity; BiS_2-superconductor; Scanning tunneling microscopy (STM)

1. Introduction

It is well known that the superconductors with the layered structure such as cuprates and iron-based superconductors show the high temperature superconductivity and the novel electronic structure. Thus, the layered superconductors are paid much attention in the condensed matter physics. Newly discovered BiS_2-based superconductors have a layered structure composed of the conductive BiS_2 layers and non-conductive block layers [1-15]. Up to now, 13 materials which have different block layers have been found in the BiS_2-based family. Among them, $LnOBiS_2$ (Ln = La, Pr, Ce, Nd, Sm, Yb, and Bi) show superconductivity by the substitution of F^- ions for O^{2-}

* Corresponding author. Tel.: +08-3-3260-4271; fax: +08-3-5261-8475.
E-mail address: demura@rs.tus.ac.jp

Peer-review under responsibility of the ISS 2015 Program Committee
doi:10.1016/j.phpro.2016.04.021

ions. The substitution of F^- ion induces not only carrier doping but also the structural change. It has been pointed out that the superconducting transition temperatures of these materials are sensitive to the crystal structure [16,17]. Furthermore, these materials have been pointed out that there is instability against the formation of charge density wave [18-20]. Thus, the measurements which clarify the structure are crucial in the study of these materials. In fact, the novel electronic structure, so-called "checkerboard stripe" structure, has been observed on the surface of the single crystalline $NdO_{0.7}F_{0.3}BiS_2$ using scanning microscopy (STM) and spectroscopy (STS) measurement [21].

Here, we report on the F concentration dependence of the surface structure of BiS_2-based superconductor $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) by STM. Square lattice consisted of Bi atoms was observed successfully on the surface of single crystalline $CeO_{0.5}F_{0.5}BiS_2$. Furthermore, an additional structure was observed on the surface of the $CeO_{0.3}F_{0.7}BiS_2$ single crystal.

2. Experimental

Single crystalline samples of $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7) were synthesized by a CsCl/KCl flux method in evacuated quarts tubes [22,23]. Mixtures of Bi, Bi_2S_3, Bi_2O_3, BiF_3, and Ce_2S_3 were ground with nominal compositions of $CeO_{1-x}F_xBiS_2$ (x = 0.5, and 0.7). Bi_2S_3 was obtained by sintering the mixtures of Bi and S in the evacuated quartz tube at 500 °C for 10 hours. The mixture of 0.8 g was mixed with CsCl/KCl powder of 5 g, and sealed in an evacuated quartz tube. The tube was heated at 800 °C for 10 hours and cooled down to 600 °C. After this thermal process, the sintered materials were washed by distilled water to remove the flux. Scanning tunneling microscopy (STM) measurements were performed at 4 K in the He gas using a laboratory-build scanning tunneling microscope. A surface of single crystals was prepared by cleaving the sample at 4K in situ. A bias voltage was applied to the sample in all measurements.

3. Results

Figure 1 shows the STM image of the surface structure on the single crystalline $CeO_{0.5}F_{0.5}BiS_2$. The square lattice with a period of approximately 4 Å can be seen in the surface structure (see Fig. 1(b)). This period is corresponding to the lattice parameter a of $CeO_{0.5}F_{0.5}BiS_2$ [4,24]. Because the cleavage occurs between two BiS_2 layers which bond weakly through Van der Waals force, the exposed surface is BiS_2 layer. The observed atoms are considered to be Bi ions as was reported in $NdO_{0.7}F_{0.3}BiS_2$ single crystal [21,25]. In addition to the periodic lattice, there are several defects of the Bi ions. The ratio of the defects is approximately 2% in the observed area shown in Fig. 1(a). Near the defects, there exist the streaks along the each diagonal direction of the square lattice, as shown in white arrows in the Fig. 1(b). These defects and streaks are also reported in $NdO_{0.7}F_{0.3}BiS_2$, though the ratio of the defects is slightly larger in $NdO_{0.7}F_{0.3}BiS_2$. Thus, the replacement of the block layer from $NdO_{0.7}F_{0.3}$ to $CeO_{0.5}F_{0.5}$ does not change the surface structure of the BiS_2 layer a lot.

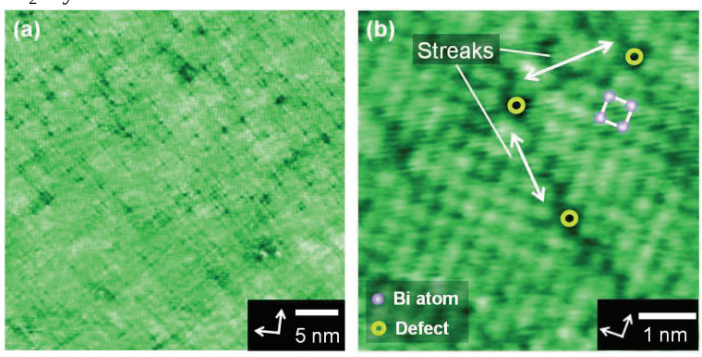

Fig. 1 (Color online)
(a) STM image at the bias voltage of 500 mV on the surface for single crystal of $CeO_{0.5}F_{0.5}BiS_2$. (b) STM image of another area in $CeO_{0.5}F_{0.5}BiS_2$ at the bias voltage of 800 mV. The filled circles formed the square are Bi atoms. The unfilled circles and white arrows show defects, and streaks, respectively.

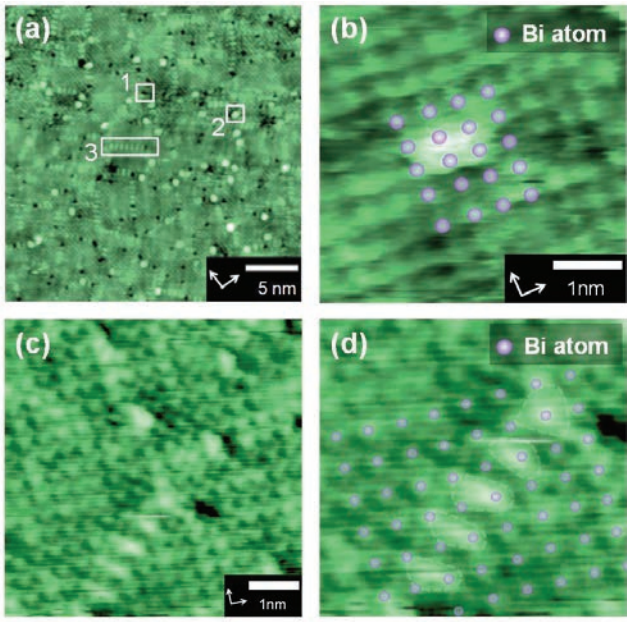

Fig. 2 (Color online)

(a) The STM image on the surface structure for single crystalline $CeO_{0.3}F_{0.7}BiS_2$. The number 1, 2, and 3 show the notable structure of defects, bright spots and bone structures. (b) The magnified figure for the one bright spot. The spheres show the Bi atoms. (c) The STM image for the one bone structure. (d) The magnified figure about the bone structure.

Next, we observed the surface of $CeO_{0.3}F_{0.7}BiS_2$, which has higher F concentration. Figure 2(a) shows the STM image of a surface structure on single crystalline $CeO_{0.3}F_{0.7}BiS_2$ at the bias voltage of 500 mV. The observed surface was quite different from that of $x = 0.5$. There are three features in the figure. One is the defects. The approximately 3% defects (indexed as 1 in Fig. 2(a)) are confirmed on the surface. Because this density of the defects is the almost same as that of $CeO_{0.5}F_{0.5}BiS_2$, it is thought that the existence of the Bi defects is independent of the F concentration. On the other hand, the streak is not seen on this surface.

The second feature is the bright spots (indexed as 2 in Fig. 2(a)). The bright spots are located randomly on the Bi plane. The density of the bright spots is approximately 0.6 %. Figure 2(b) shows the enlarged figure of the one bright spot. The size of bright spot is about 2 x 3 times of Bi atoms.

The third feature is the structure resembled to “backbone” (indexed as 3 in Fig. 2(a)). This structure is termed to “bone” structure in the following. Figure 2(c) shows the one of the bone structure. This structure consists of the row of a few triangular components as shown in Fig. 2(c) and (d). The bone structure tends to exist near the defects of Bi atom and is along the both of the diagonal directions of the square lattice. The number of bone structures in Fig. 2 (a) is approximately 45, and 7 % of the surface is covered by the bone structures.

Although the origin of the bright spots or the bone structures observed on the F rich sample is not sure, there are some possibilities about the origin of these structures. One is the absorption of atoms or clusters on the surface. For example, the Bi atom missed from the top most layer is a candidate. However, this is not the case because the number of the missed Bi atoms cannot account for the number of the surface structures whose size is larger than the Bi atom. K or Cs ions, which were included in the flux KCl and CsCl used to synthesize these single crystals, are also a candidate. However, as the sample with the low F concentration, which was also made with these fluxes, does not show such surface structures, it is also impossible to be a origin. Thus, the surface structures are not considered to the absorbed atoms or clusters.

Another possibility is the formation of the structural deformation to relax the structure. In samples with the low F concentration, there exist streaks along the diagonal directions of the square lattice. Instead, in the sample with high

F concentration, the bone structures appear along the diagonal directions. Thus, the observed bone structure and the bright spots may appear due to the structural deformation to relax the structure caused by high F doping. It is noted that the underlying instability exists along these directions because some theories predict the charge density wave instability along the diagonal direction [18]. In fact, “checkerboard stripe” structure appeared in this direction [21]. To reveal this possibility, the further measurements for the electronic structure are needed.

4. Summary

we observed the surface structure on single crystalline $CeO_xF_{1-x}BiS_2$ (x = 0.5, and 0.7). In the sample with x = 0.5, the surface structure consisted of the square lattice of Bi atoms was observed. The sample with x = 0.7 shows the bright points and the bone structures on the surface. These findings indicate that the surface structure is changed by the increase in the F concentration of the sample.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (KAKENHI).

References

[1] Y. Mizuguchi *et al*., Phys. Rev. B **86** (2012) 220510(R).
[2] Y. Mizuguchi *et al*., J. Phys. Soc. Jpn. **81** (2012) 114725.
[3] S. Demura et *al*., J. Phys. Soc. Jpn. **82** (2013) 033708.
[4] J. Xing *et al*., Phys. Rev. B **86** (2012) 214518.
[5] R. Jha *et al*., J. Sup. and Novel Mag. **26** (2013) 499.
[6] D. Yazici *et al*., Philosophical Magazine **93** (2012) 673.
[7] D. Yazici et *al*., Phys. Rev. B **87** (2013) 174512.
[8] X. Lin et *al*., Phys. Rev. B **87** (2013) 020504(R).
[9] A. Krzton-Maziopa et *al*., J. Phys.: Condens. Matter **26** (2014) 215702.
[10] G. S. Thakur *et al*., Inorg. Chem. **54** (2015) 1076.
[11] H. Lei *et al*., Inorg. Chem. **52** (2013) 10685.
[12] X. Lin *et al*., Phys. Rev. B **87** 1 (2013).
[13] H. F. Zhai et *al*., Phys. Rev. B **90** (2014) 064518.
[14] H. F. Zhai et *al*., J. American Chem. Soc. **136** (2014) 15386.
[15] J. Shao et *al*., : Supercond. Sci. Technol. **28** (2015) 015008.
[16] Y. Mizuguchi, J. Phys. Chem. Solids **84** (2015) 34.
[17] D. Yazici *et al*., Physica C **514** (2015) 218.
[18] H. Usui *et al*., Phys. Rev. B **86** (2012) 1.
[19] T. Yildirim, Phys. Rev. B **87** (2013) 020506.
[20] H. F. Zhai et *al*., Phys. Rev. B **90** (2014) 064518**.**
[21] T. Machida et *al*., . Phys. Soc. Jpn. **83** (2014) 113701.
[22] M. Nagao et *al*., J. Phys. Soc. Jpn. **81** (2012) 103702.
[23] M. Nagao et *al*., Solid State. Commun. **178** (2014) 33.
[24] S. Demura, et *al*., J. Phys. Soc. Jpn. **84** (2015) 024709.
[25] S. Demura, Solid. State. Comm. **223** (2015) 40.